Thermodynamics Lecture Notes: Chapter 4

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4 Statistical thermodynamics I: Kinetic Gas Theory

4.1 Microscopic view of temperature

In this section, we try to describe the equation of the state of gas from the microscopic view, i.e. as an ensemble of particles with an identical mass moving in random directions isotropically in container (see figure below). We assume that there is no interaction between the particle and the wall of the container, containing the gas, nor between the particles themselves. When a particle collides with the wall or with other particles, it makes an elastic scattering.

The gas is in a cubic container, as shown in the figure. The pressure, P, of the gas acting on the container wall is caused by the elastic scattering of the gas molecules with the wall.

Let us consider first that there is only one gas molecule in the container. The force acting on the wall A by the molecule through the elastic scattering can be given by

$$\frac{\Delta p}{\Delta t} \tag{1}$$

where Δp is the momentum change of the molecule within the time interval Δt. In the scattering process, only the x-component of the velocity changes from v_x to $-v_x$ and the time interval to have one scattering corresponding to the time needed to traverse for the molecule from A to B and back to A. It follows that
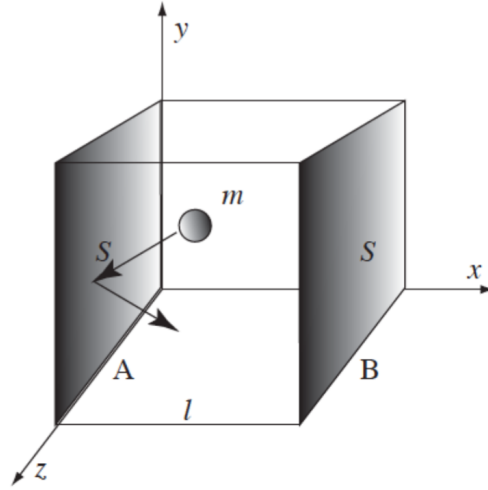
$$\Delta p = -mv_x - mv_x = -2mv_x, \quad \Delta t = \frac{2l}{v_x} \tag{2}$$

leading to

$$\frac{\Delta p}{\Delta t} = \frac{-2mv_x}{2l/v_x} = -\frac{mv_x^2}{l} \tag{3}$$

The force onto the wall is then

$$F = \frac{mv_x^2}{l}. \tag{4}$$

Now we consider the case, where we have a large number of N molecules within the container. The force then becomes:

$$F = \frac{m \sum_{i=1}^{N} (v_x^i)^2}{l}. \tag{5}$$

By introducing the average of v_x^2, given by

$$\langle v_x^2 \rangle = \frac{\sum_{i=1}^{N} (v_x^i)^2}{N} \tag{6}$$

the force given by

$$F = \frac{Nm\langle v_x^2 \rangle}{l} \tag{7}$$

Recalling $v_x^2 + v_y^2 + v_z^2 = v^2$, it follows that

$$\langle v^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \left[(v_x^i)^2 + (v_y^i)^2 + (v_z^i)^2 \right] = \frac{1}{N} \left(\sum_{i=1}^{N} (v_x^i)^2 + \sum_{i=1}^{N} (v_y^i)^2 + \sum_{i=1}^{N} (v_z^i)^2 \right) \tag{8}$$
$$= \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

If the movement of the gas molecules is random and isotropic, $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$, we have

$$\langle v_x^2 \rangle = \frac{\langle v^2 \rangle}{3} \tag{9}$$

and

$$F = \frac{Nm\langle v^2 \rangle}{3l}. \tag{10}$$

By denoting the area of the wall A to be S, the pressure is given by

$$P = \frac{F}{S} = \frac{Nm\langle v^2 \rangle}{3lS} = \frac{Nm\langle v^2 \rangle}{3V} \tag{11}$$

where V is the volume of the container. It follows that

$$PV = \frac{2}{3} N \left(\frac{1}{2} m \langle v^2 \rangle \right) = \frac{2}{3} N \langle K \rangle \tag{12}$$

where $\langle K \rangle = \frac{1}{2} m \langle v^2 \rangle$ is the average of the kinetic energy of the gas molecule. By comparing this to the equation of the state for the ideal gas,

$$PV = NkT. \tag{13}$$

we can conclude

$$\langle K \rangle = \frac{3}{2} kT \tag{14}$$

i.e. the average kinetic energy of the molecule of an ideal gas is directly proportional to the absolute temperature.

Examples:

- **What is the average kinetic energy of an ideal gas molecule at $37°C$?**
  Noting that $37°C$ is $310K$, we obtain

$$\langle K \rangle = \frac{3}{2}kT = \frac{3}{2}1.38 \times 10^{-23}J/K \times 310K = 6.42 \times 10^{-21}J \qquad (15)$$

For one mole of molecules, the kinetic energy becomes

$$N_A \langle K \rangle = 6.02 \times 10^{-23} \times 6.42 \times 10^{-21}J = 3860J \approx 1\text{kcal} \qquad (16)$$

- **How fast are molecules (O_2 and N_2) moving at room T?**
  The root-mean-squared velocity of an ideal gas molecule at an absolute temperature T is then given by

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{2\langle K \rangle}{m}} = \sqrt{\frac{3kT}{m}}. \qquad (17)$$

The root-mean-squared velocity of O_2 (molecular mass 32 u) and N_2 (molecular mass 28 u) at $37°C$ can be calculated using the above equation. Since 1 u corresponds to $1.66 \times 10^{-27}kg$, the masses of one molecule for them are given by

$$\begin{aligned} m(O_2) &= 32 \cdot 1.66 \times 10^{-27}kg = 5.3 \times 10^{-26}kg \\ m(N_2) &= 28 \cdot 1.66 \times 10^{-27}kg = 4.6 \times 10^{-26}kg \end{aligned} \qquad (18)$$

and

$$\begin{aligned} v_{rms}(O_2) &= \sqrt{\frac{3kT}{m(O_2)}} = \sqrt{\frac{3.1.38 \times 10^{-23}J/K.293K}{5.3 \times 10^{-26}kg}} = 480m/s \\ v_{rms}(N_2) &= \sqrt{\frac{3kT}{m(N_2)}} = \sqrt{\frac{3.1.38 \times 10^{-23}J/K.293K}{4.6 \times 10^{-26}kg}} = 510m/s \end{aligned} \qquad (19)$$

Note that the lighter a gas molecule is, the faster it moves at a same temperature.

4.2 Special Exercise I: Two subsystems of ideal gas

An isolated system of volume V_0 consists of two subsystems, labelled 1 and 2, separated by an impermeable (no particle flow) and moving diathermal (exchange of heat) wall of mass M and of negligible volume. Both subsystems contain ideal gas. Initially, both subsystems are at the temperature T_i. Subsystem 1 is in a state characterised by a volume V_{1i} and Pressure P_{1i}. Likewise, subsystem 2 is characterised by a pressure P_{2i} and volume V_{2i}. When the system has reached equilibrium the final temperature is equal to the initial temperature. Determine:

1. The number of moles n_1 and n_2 of in both subsystems.

2. The final volumes V_{1f} and V_{2f} of the subsystems when the system has reached equilibrium.

3. The final pressure P_f when the system has reached equilibrium.

4. The kinetic energy of the subsystem and the total system in equilibrium.

Solution:

1. *Since the wall is impermeable, the numbers of moles are constant. Thus:*

$$n_1 = \frac{P_{1i}V_{1i}}{RT_i} \text{ and } n_2 = \frac{P_{2i}V_{2i}}{RT_2}$$

2. *Given that the wall is movable, in equilibrium, not only the temperatures will be the same, but also the pressure P. Owing to the equation of state for each subsystem, also in the final state, we have:*

$$P_f V_{1f} = n_1 RT_f \text{ and } P_f V_{2f} = n_2 RT_f$$

Similarly, the equation of state for the entire system in the final state is given by:

$$P_f V_0 = (n_1 + n_2)RT_f$$

with V_0 being the sum of the subvolumes. Solving this equation for P_f and inserting the expression in the equation of state of each subsystem, we obtain the final volumes:

$$V_{1f} = \frac{n_1}{n_1 + n_2}V_0 \text{ and } V_{2f} = \frac{n_2}{n_1 + n_2}V_0$$

3. *The final pressure is given by:*

$$P_f = \frac{(n_1 + n_2)RT_f}{V_0}$$

It is the pressure of gas of $n_1 + n_2$ moles at temperature T_f occupying the volume V_0 of the whole system.

4. *According the kinetic theory of gas, the average kinetic energy of ideal gas is only dependent on the temperature of the gas. Since the final temperature in the two subsystem is the same, also the average kinetic energy (per molecule) is the same:*

$$\langle K_1 \rangle = \langle K_2 \rangle = \frac{3}{2}kT_f$$

Since the kinetic energy is an extensive quantity (additive), the kinetic energy of the whole system is:

$$K = n_1 N_A \langle K_1 \rangle + n_2 N_A \langle K_2 \rangle = (n_1 + n_2)N_A \langle K \rangle = \frac{3}{2}(n_1 + n_2)RT_f \text{ (with } R = kN_A)$$

4.3 Special exercise II: Atmosphere composition on planets

1. The escape velocity on Mars is 5 km/s and the temperature on its surface is 0°C. Compute for this temperature v_{rms} of H_2, O_2 and CO_2. If v_{rms} is greater than roughly one sixth of the escape velocity, then the gas will not be retained in the atmosphere of the planet. Which of the listed gases will remain in the Mars atmosphere under this condition?

2. Repeat the same analysis for Jupiter; note that its escape velocity is 60 km/s and its surface temperature is -150°C.

3. The escape velocity of planet earth with Radius R (6378km) can be calculated via $v_e = \sqrt{2gR}$, where g is the acceleration on earth.

   (a) At which temperature is v_{rms} of O_2 and of H_2 equal to the escape velocity on earth?

   (b) In the upper atmosphere is the temperature is the temperature roughly 1000K. What does this imply on the existence of oxygen in the upper atmosphere?

   (c) Compute the temperatures, for which v_{rms} of O_2 and H_2 is equal to the escape velocity on the moon, which has an acceleration of roughly one sixth of that on earth (the radius of the moon is 1738 km). Why does the moon not have an atmosphere (assume for simplicity that the T on the moon is similar as in the upper atmosphere of the earth)?

Solution:

1. v_{rms} is given by $\sqrt{3kT/m}$. T is 273 K. The masses of H_2, O_2 and CO_2 are $m_{H_2} = 2 \times 1.7 \cdot 10^{-27} kg$, $m_{O_2} = 32 \times 1.7 \cdot 10^{-27} kg$ and $m_{CO_2} = 44 \times 1.7 \cdot 10^{-27} kg$. Thus:

   $$v_{rms,H_2} = 1846 \ m/s, \ v_{rms,O_2} = 461 \ m/s, \ v_{rms,CO_2} = 393 \ m/s.$$

   One sixth of the escape velocity on Mars is 833 m/s. Thus, O_2 and CO_2 exist in the atmosphere of Mars, but no Hydrogen.

2. The calculation is the same as in 1., but now for a temperature of $T = 123.15$ K. Inserting the masses and the temperature into the expression for v_{rms}, we obtain:

   $$v_{rms,H_2} = 1239 \ m/s, \ v_{rms,O_2} = 310 \ m/s, \ v_{rms,CO_2} = 264 \ m/s.$$

   One sixth of the escape velocity of Jupiter is 10^4 m/s. Thus, for Jupiter all of the considered gases can be in its atmosphere.

3. If we solve the above expression of v_{rms} for T, we obtain: $T = \frac{m v_{rms}^2}{3k}$.

   (a) On earth is $v_{rms}^2 = v_e^2 = 2gR_e$ with R_e being the radius of the earth. Thus, we obtain for T:
   $$T = \frac{2mgR_e}{3k}.$$
   Using the values for the masses of oxygen and hydrogen as written above, we obtain $T = 1.6 \cdot 10^5 K$ and $T = 1.0 \cdot 10^4 K$ for oxygen and hydrogen, respectively, at which the rms velocity is equal to the escape velocity.

   (b) For oxygen, the temperature in the upper atmosphere is too low so that oxygen molecules do not have a high enough kinetic energy/average velocity to leave.

   (c) On the moon, $g = 9.81/6 \ m/s^2$, and with its radius $R_m = 1738$ km, we can compute the escape velocity $v_m = 2.38 \cdot 10^3$ m/s. With the same equation as before, we can estimate the temperate for which v_{rms} of hydrogen and oxygen is equal to the escape velocity. For hydrogen and oxygen, we obtain $T \sim 7.3 \cdot 10^3$ K and ~ 460 K. If we assume that the temperature on the moon is similar to that of the upper earth atmosphere (1000K), then it is clear that that both gases cannot be retained by the gravity field of the moon.